# <Division of Materials Chemistry> Chemistry of Polymer Materials

# Division of Materials Chemistry
## - Chemistry of Polymer Materials -

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### Visitors

| | |
|---|---|
| Prof FUJIKAWA, Seizo | Hokkaido University, 26 March 2009 |
| Prof WATANABE, Junji | Tokyo Institute of Technology, 27 March 2009 |

## Scope of Research

Kinetic and mechanistic analyses are made for better understandings of the chemical and physicochemical reactions occurring in polymerization systems and for better routes to the synthesis of well-defined polymers. By various polymerization techniques, in particular, living polymerizations, new well-defined polymers or polymer assemblies are prepared, and their structure/properties relationships are precisely analyzed. Projects in progress include: (1) kinetics and mechanisms of living radical polymerization (LRP). (2) Synthesis of new polymeric materials by living polymerizations and their structure/properties studies. (3) Synthesis, properties, and applications of concentrated polymer brushes (CPB).

## Research Activities (Year 2009)

### Publications

Tsujii Y, Nomura A, Okayasu K, Gao W, Ohno K, Fukuda T: AFM Studies on Microtribology of CPBs in Solvents, *J. Phys: Conf. Ser.* **184**, no. 012031 (2009).

Ladmiral V, Morinaga T, Ohno K, Fukuda T, Tsujii Y: Synthesis of Monodisperse Zinc-Sulfide Particles Grafted with CPB by Surface-Initiated Nitroxide-Mediated Polymerization, *Eur. Polym. J.*, **45**, 2788-2796 (2009).

Goto A, Nagasawa K, Tsujii Y, Fukuda T: Reversible Chain Transfer Catalyzed Polymerization (RTCP) with Alcohol Catalysts, *ACS Symp.*, **1023**, 159-168 (2009).

### Presentations

Tsujii Y, New Development of CPBs as Novel Interfaces, NSYSU-KU Bilateral Symposium on Materials Chemistry, Kaohsiung, Taiwan, 22–23 September.

Ohno K, Applications of CPB/Particle Hybrids, PPC11, Carins, Australia, 6–10 December.

Goto A, RTCPs with P, N, and O Catalysts. Materials of the Future, Melbourne, Australia, 15–17 February.

16 presentations, CPB meeting, Kyoto, 27 March.

6 Presentations, 58th Autumn Meeting, Soc. Polym. Sci., Jpn., Kumamoto,16–18 September.

### Grants

Tsujii Y, Fabrication of Novel Tribomaterials and Their Structural Analyses, Grant-in-Aid for Science Research (A), 1 April 2009–31 March 2012.

Tsujii Y, Development of High-Performance Battery System for Next-Generation Vehicles by NEDO, 1 July 2007–30 November 2009.

Tsujii Y, R&D of High-Efficient Organic Thin-Film Solar Cell with Supra-Hierarchical Nano-Structure, R&D for Next Generation PV System Technologies by NEDO,

## Super-Lubrication Mechanism of Concentrated Polymer Brushes in Solvents

Previously, we revealed the super lubrication (ultra-low friction) between concentrated polymer brushes (CPBs) in good solvent. In order to clarify the lubrication mechanism in detail, the frictional coefficient $\mu$ was measured as a function of shearing speed $v$ and solvent quality (controlled by mixing good and poor solvents), suggesting two mechanisms for swollen brushes; one is the boundary lubrication (with $\mu$ data little dependent on $v$), in which the non-interpenetrating interaction between the confronted brushes (specific to the CPB) plays an important role for ultra-low friction. The other is the hydrodynamic lubrication (with $\mu$ data dependent on $v$), in which the frictional property is related to the viscosity of solvent; interestingly, the data in this regime could be scaled by the degree of swelling. The better understanding of lubrication mechanism would open up a new strategy for the creation of novel tribomaterials.

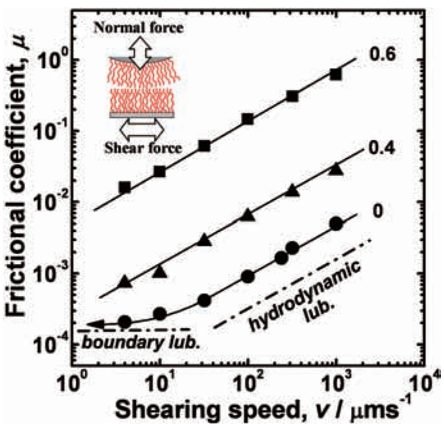


**Figure 1.** Plot of frictional coefficient $\mu$ vs shearing speed $v$ for the CPB of poly(styrene) in isopropanol(IPA)/toluene(TOL) mixtures; the figures indicate the IPA content.

## Carbon-Centered Compounds as a Novel Class of Catalysts for a Living Radical Polymerization

Carbon-centered compounds were successfully used as a novel class of catalysts for a living radical polymerization (RTCP). Low-polydispersity polystyrenes and functional polymethacrylates with predicted molecular weight were obtained with a fairly high conversion in a fairly short time. Notably, the catalysts include such common compounds as 1,4-cyclohexadine (CHD) and diphenyl methane (DPM). Their commonness (hence low cost) and environmental safety may be attractive for practical applications. They also exhibited good tolerance to functional groups, being useful to a variety of functional monomers.

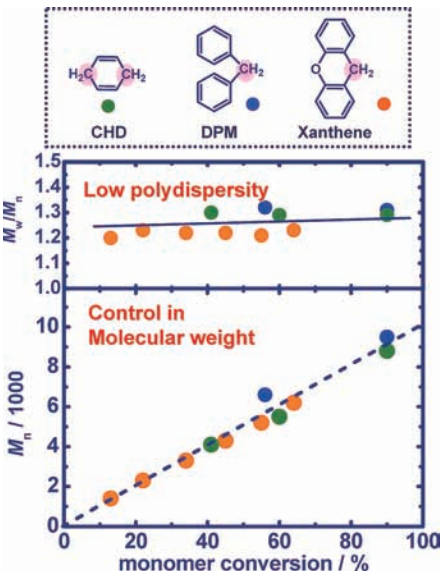


**Figure 2.** Plots of molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) vs monomer conversion for the polymerizations of methyl methacrylate with carbon-centered catalysts.

1 September 2006–20 March 2010.

Tsujii Y, Development of Technology for Next-generation Fuel Cells by NEDO, 1 September 2008–20 March 2010.

Tsujii Y, Development of Novel Nanosystems by Hierarchically Assembling CPBs, CREST Program by JST, 1 October 2009–31 March 2015.

Ohno K, Development of Next-Generation MRI Contrast Agent, Industrial Technology Research Grant Program by NEDO, 1 July 2009–30 June 2013.

Goto A, Non-Transition-Metal Catalyzed and Photo-Induced LRPs, Grant-in-Aid for Young Scientists (B), 1 April 2007–31 March 2009.

Goto A, Development of Green LRP with Low Cost, Industrial Technology Research Grant Program by NEDO, 10 September 2007–31 August 2011.

Goto A, Development of New LRP, JST Promotion of Technology Research Partnership, 10 August 2008–31 July 2009.

Goto A, Fundamentals and Applications of New LRP, Kyoto Univ. Step Up Research Grant, 4 June 2009–31 March 2010.